

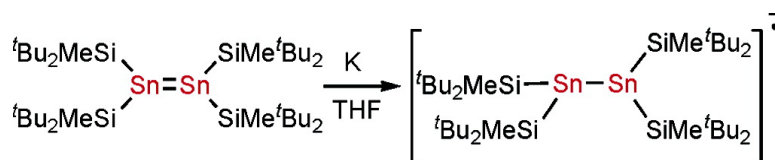
Communication

Tetrakis(di-*tert*-butylmethylsilyl)distannene and Its Anion Radical

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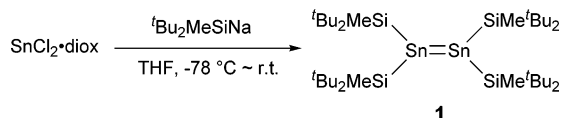
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The chemistry of distannenes $>Sn=Sn<$, the doubly bonded derivatives of tin atoms, has the longest history among all heavy alkene analogues of the type $>E=E'<$ (E, E' are group 14 elements).¹ The first stable compound with an $Sn=Sn$ double bond, $[(Me_3Si)_2CH]_2Sn=Sn[CH(SiMe_3)_2]_2$, was reported nearly 30 years ago by Lappert et al.² However, all distannenes ($R_2Sn=SnR_2$) known to date, although indefinitely stable in the solid state, dissociate in solution into two stannylenes (R_2Sn).²⁻⁵ In this communication, we report the synthesis of the first acyclic distannene that is stable both in the solid state and in solution, as demonstrated by its reactivity. The reduction of this distannene with alkali metal produced its corresponding isolable anion radical, which has been fully characterized by X-ray crystallography and ESR spectroscopy.

The distannene **1** was synthesized by the coupling reaction of $tBu_2MeSiNa$ and $SnCl_2$ -diox in THF at room temperature and was isolated as air- and moisture-sensitive dark-green crystals in 43% yield (Scheme 1).^{6,7} **1** was characterized by a full range of spectral and analytical data, of which the most important is the downfield-shifted resonance of the sp^2 Sn atoms at +630.7 ppm.^{6,8}

Scheme 1



The crystal structure of distannene **1** was determined by X-ray crystallography (Figure 1), which showed several diagnostic

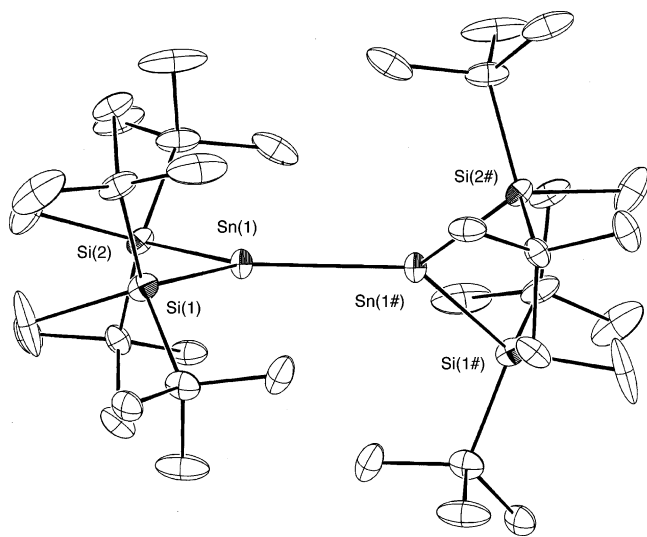
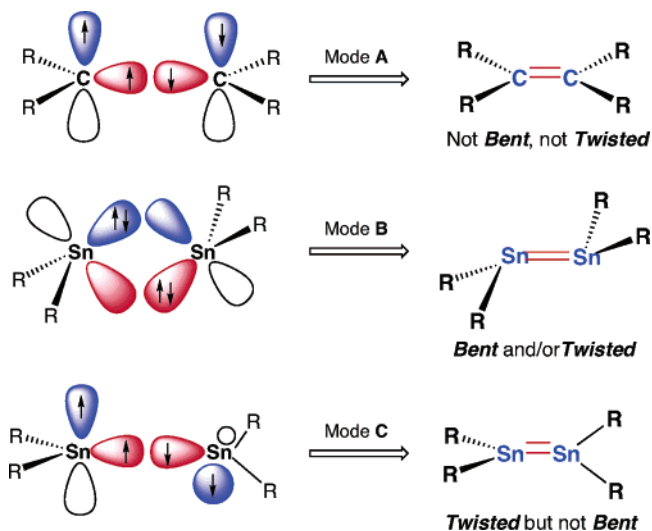


Figure 1. ORTEP drawing of **1**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): $Sn(1)-Sn(1\#) = 2.6683(10)$, $Sn(1)-Si(1) = 2.631(2)$, $Sn(1)-Si(2) = 2.630(2)$. Selected bond angles (deg): $Si(1)-Sn(1)-Si(2) = 109.27(8)$, $Si(1)-Sn(1)-Sn(1\#) = 124.21(7)$, $Si(2)-Sn(1)-Sn(1\#) = 126.50(5)$.

structural features.⁹ First, the $Sn=Sn$ bond length is very short, 2.6683(10) Å, being the shortest one among all acyclic distannenes.^{2,3} Second, the sp^2 Sn atoms have planar geometry: the sum of the bond angles around them is 359.98°; thus, the bend angle is only 1.22(5)°. This is in sharp contrast to all other distannenes whose crystal structures have been reported to date: all of them have a highly pronounced trans bent configuration of the substituents (from 21.4 to 64.4°).^{2,3} The final striking structural peculiarity is the significant twisting of the $Sn=Sn$ double bond (twist angle of 44.62(7)°), which definitely can be ascribed to the great steric congestion due to the bulky tBu_2MeSi substituents. Such a combination of the planarity around the sp^2 Sn atoms and the twisting of $Sn=Sn$ double bond is rather unusual in the structural chemistry of heavy alkenes. Neither of the two commonly accepted double bond models,^{3a} interaction of the two triplet carbenes providing a planar $C=C$ double bond (Chart 1, A) or donor–

Chart 1

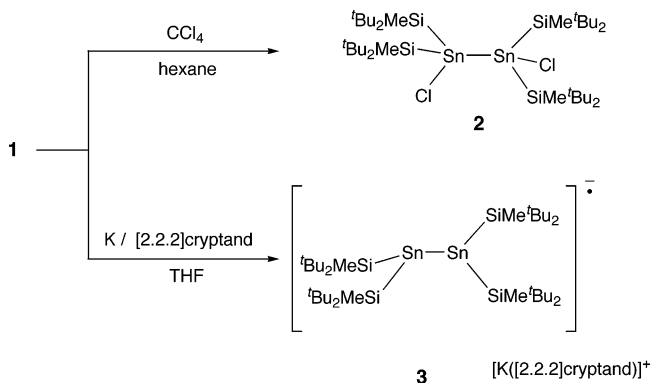


acceptor interaction of the two singlet stannylenes to form a dative $Sn=Sn$ bond with trans bending of substituents (Chart 1, B), adequately describes the bonding situation in **1**. Apparently, in this particular case, one should explain the formation of the $Sn=Sn$ double bond as a result of the *out-of-plane* (rather than *in-plane*, A) interaction of the two triplet stannylenes, resulting in the formation of the highly *twisted* but *not bent* $Sn=Sn$ bond (Chart 1, C). Such a bonding motif is quite unusual in the structural chemistry of distannenes. The shortening and planarization of the $Sn=Sn$ double bond in **1** should be attributed to the influence of the four σ -donating silyl substituents.^{1a}

Even being highly strained, distannene **1** does not dissociate in solution, in contrast to all other acyclic distannenes. The manifestation of the real $Sn=Sn$ double bond in the solution of **1** was clearly demonstrated by the ^{119}Sn NMR chemical shift of +630.7 ppm,

which lies in the region expected for doubly bonded Sn atoms, and well outside the typical chemical shifts of stannylenes.⁸ This was definitely proved by the reactivity of **1**: it immediately reacts with CCl₄ to form the corresponding 1,2-dichloro adduct **2** in a high yield (Scheme 2).⁶ Thus, **1** represents the first acyclic distannene that preserves its Sn=Sn double bond in both the solid and solution states.

Scheme 2



One can expect that distannene **1** should be easily reduced with alkali metals because of its low-lying and easily accessible LUMO. Indeed, the reduction of **1** with potassium mirror in the presence of [2.2.2]cryptand resulted in the immediate formation of the corresponding distannene anion radical **3**, isolated as extremely sensitive red cubic crystals in 66% yield (Scheme 2).⁶ The structure of this very unusual compound, representing a stable ion radical of the alkene analogues of heavier group 14 elements, was fully elucidated in both the solid and solution states.¹⁰ The crystal structure of **3** displayed the highly twisted (twist angle 73.63(6)°) Sn–Sn bond with a bond length of 2.8978(3) Å, which is 0.2295 Å longer than that in starting distannene **1** (Figure 2).^{9,11} The



Figure 2. ORTEP drawing of **3**. The cationic part of the molecule (potassium cation complexed with [2.2.2]cryptand) and hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Sn(1)–Sn(2) = 2.8978(3), Sn(1)–Si(1) = 2.6679(8), Sn(1)–Si(2) = 2.6781(8), Sn(2)–Si(3) = 2.6432(9), Sn(2)–Si(4) = 2.6507(9). Selected bond angles (deg): Si(1)–Sn(1)–Si(2) = 109.81(3), Si(1)–Sn(1)–Sn(2) = 107.51(2), Si(2)–Sn(1)–Sn(2) = 105.836(19), Si(3)–Sn(2)–Si(4) = 113.66(3), Si(3)–Sn(2)–Sn(1) = 107.34(2), Si(4)–Sn(2)–Sn(1) = 134.39(2).

geometry of both Sn atoms is different: one of them adopts a highly pyramidal configuration (sum of the bond angles 323.16°, trans bend angle 60.05(4)°), whereas the other atom is essentially planar (sum of the bond angles 355.39°, trans bend angle 19.50(4)°). One can reasonably assume that both the negative charge and the unpaired electron are effectively separated between the two tin atoms in the solid-state structure of **3**.

It is particularly interesting that such a charge–electron separation is also maintained in the solution of **3**. This was demonstrated by the ESR spectrum of **3**, which showed an intense central signal ($g = 2.0517$) with two pairs of satellites due to the coupling of the unpaired electron with α - and β -^{119,117}Sn atoms with the hyperfine coupling constant (hfcc) values of $a(\alpha\text{-}^{119,117}\text{Sn}) = 34.0$ mT and $a(\beta\text{-}^{119,117}\text{Sn}) = 18.7$ mT, respectively.^{12,13} This implies the localization of a single electron on one of the two Sn atoms, that is, separation of the anion and radical parts of the molecule in solution.

Supporting Information Available: Experimental procedures and spectral data for **1**, **2**, and **3**, and tables of crystallographic data including atomic positional and thermal parameters for **1** and **3** (CIF, PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- The only distannene stable in solution is cyclotristannene (ref 3g), which is very different from the acyclic distannenes case.
- The weakness of the >Sn=Sn< double bond was attributed to the lower attraction and decreased localization of the valence shell electrons into the bonding region because of the larger size and lower electronegativity of the tin atoms, according to ELF and AIM calculations. See: Malcolm, N. O. J.; Gillespie, R. J.; Popelier, P. L. A. *J. Chem. Soc., Dalton Trans.* **2002**, 3333.
- For the experimental procedures and spectral data of **1**, **2**, and **3**, see Supporting Information.
- When we used Et₂O instead of THF, a completely different product, tris-(di-*tert*-butylmethylsilyl)stannyl radical, was formed upon the reaction of ^tBu₂MeSiNa with SnCl₂·diox. See: Sekiguchi, A.; Fukawa, T.; Lee, V. Ya.; Nakamoto, M. *J. Am. Chem. Soc.* **2003**, *125*, 9250.
- Both low and high temperature ¹¹⁹Sn NMR spectra of **1** did not show any signs of >Sn=Sn< bond dissociation, since no resonances of stannylene species were observed. Previously, the variable temperature of ¹¹⁹Sn and ¹³C NMR spectra of [(Me₃Si)₂CH]₂Sn=Sn[CH(SiMe₃)₂]₂ both in solution and in the solid state (CP-MAS) were reported. See: Zilm, K. W.; Lawless, G. A.; Merrill, R. M.; Millar, A. M.; Webb, G. G. *J. Am. Chem. Soc.* **1987**, *109*, 7236.
- For the crystal data for **1** and **3**, see Supporting Information.
- A related distannene anion radical ArSnSnAr[−] (Ar = 2,6-bis-(2,4,6-*Pr*₃C₆H₂)C₆H₃) with a delocalized anion radical system was recently reported. See: Olmstead, M. M.; Simons, R. S.; Power, P. P. *J. Am. Chem. Soc.* **1997**, *119*, 11705.
- The elongation of the Sn–Sn bond is certainly due to the change in the bond order upon one-electron reduction: in contrast to distannene **1** the anion radical **3** lacks double bond character.
- For the ESR spectrum of **3**, see Supporting Information.
- The satellite signals from the ¹¹⁹Sn and ¹¹⁷Sn nuclei are not separated from each other because of the very small difference between the hfccs $a(^{119}\text{Sn})$ and $a(^{117}\text{Sn})$ relative to the ESR spectrum line width (2.3 mT).

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